



Evaluation of Visual Methods to Detect NAPL in Soil and Water

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Abstract

Non-aqueous phase liquids (NAPLs), such as chlorinated solvents and petroleum products, are present in the subsurface at numerous contamination sites in North America. Determination of NAPL presence should be an early investigation goal to guide site characterization and control efforts. Indirect methods for assessing NAPL presence rely on comparing measured chemical concentrations to effective solubility limits for ground water and to calculated equilibrium partitioning concentrations for soil. Under ideal conditions, NAPL presence can be identified by visual examination of soil or ground water samples. Direct visual detection may be difficult, however, where the NAPL is clear and colorless, present at low saturation, or distributed heterogeneously. There appears to be little documentation of practical, simple methods for direct identification of NAPL in soil or water.

For this study, a series of experiments was conducted to test the hypothesis that simple and inexpensive methods can be used to visually identify clear, colorless NAPL in soil and water samples. Specific methods evaluated include direct visual examination, ultraviolet (UV) fluorescence analysis, a soil-water shake test, adding hydrophobic dye to the shake test, and centrifugation. Additionally, the utility of organic vapor analysis was examined as an NAPL screening tool.

Of the methods investigated, the hydrophobic dye methods, followed by UV fluorescence, offer the most simple, practical, and effective means for direct visual identification of clear, colorless NAPL in contaminated soil samples. These methods can be utilized in the field or in a lab with minimal time and material expense. For volatile NAPLs, analysis of organic vapors in soil sample headspace can be used to screen samples for further examination and, possibly, to infer NAPL presence. The NAPL in water experiments demonstrate that very small quantities of clear, colorless NAPL in water can be quickly identified by mixing in a tiny amount of hydrophobic dye.

Introduction

Non-aqueous phase liquids (NAPLs), such as chlorinated solvents and petroleum products, may be present in the subsurface at thousands of contamination sites in North America (U.S. EPA 1986; NRC 1990). In many cases, these NAPLs are long-term sources of ground water contamination that require special consideration during remedial activities (U.S. EPA 1992a; Mercer and Cohen 1990; and Huling and Weaver 1991). For example, precautions need to be taken to minimize the potential for inducing unwanted NAPL migration during drilling or pumping operations, and the feasibility of aquifer restoration may be significantly limited by NAPL presence (U.S. EPA 1992a).

Determination of NAPL presence should be an early investigation goal to guide the selection of methods for site characterization and control. NAPL presence may be inferred from knowledge of NAPL usage, release, or disposal at a site, and verified by examination and analysis of subsurface samples (U.S. EPA 1992b).

Indirect methods for assessing the presence of NAPL in the subsurface rely on comparing measured chemical concentrations to effective solubility limits for ground water and to calculated equilibrium partitioning concen-

trations for soil (Feenstra 1990; Feenstra et al. 1991; Sitar et al. 1990; and Mackay et al. 1991). Where present as a separate phase, NAPL compounds are generally detected at <10 percent of their aqueous solubility limit in ground water samples. This is due to the effects of non-uniform ground water flow, variable NAPL distribution, the mixing of ground water in a well, and the reduced effective solubility of individual compounds in a multicomponent NAPL mixture (Mercer and Cohen 1990). Typically, dissolved contaminant concentrations >1 percent of the aqueous solubility limit are suggestive of NAPL presence; however, concentrations less than 1 percent of the solubility limit are not necessarily indicative of NAPL absence (U.S. EPA 1992a,b).

In soil, contaminant concentrations in the percent range are generally indicative of NAPL presence. However, NAPL may also be present at much lower soil concentrations. Feenstra et al. (1991) detail an equilibrium partitioning method for assessing the presence of NAPL in soil samples based on determining total chemical concentrations, soil moisture content, porosity, organic carbon content, approximate composition of the possible NAPL, sorption parameters, and solubilities. Unfortunately, the requisite data are commonly unavail-

the fluid surface. This type of soil-water shake test can be used to identify the presence of separate fluid phases where sufficient visual contrast exists between the water, soil, and NAPL.

The subsample was then centrifuged at approximately 1250 rpm for one minute. This generally produced a fairly clear supernatant for the saprolitic silt loam and medium sand soil samples. Subsamples of silt loam topsoil, however, remained a dark suspension due to their high concentration of light organic matter. The subsamples were inspected as previously described and rated for NAPL presence.

After the centrifuge test, approximately 2 mg (an amount that would rest on the edge of a toothpick) of Sudan IV, a non-volatile hydrophobic dye, was placed in the centrifuge tube. The contents of the tube were then mixed by shaking manually for approximately 10 to 30 seconds and examined for NAPL presence. NAPL presence was rated A, B, or C, and a notation of the relative NAPL density and quantity was made when apparent.

Sudan IV is a relatively inexpensive (100 g cost \$19 from Aldrich Chemical Co.), reddish brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. Like many other solvent dyes, Sudan IV is an irritant and possible mutagen with which skin or eye contact should be avoided. Although widely used to colorize NAPL flow experiments (Schwille 1978, for example), minimal use has been made of solvent dyes such as Sudan IV and Oil Red O to detect NAPL in soil and water at contamination sites.

The final step in the soil examination procedure was to centrifuge the dyed subsample at approximately 1250 rpm for one minute, and then peer through the tube walls and at the fluid surface to assess NAPL presence and relative density and quantity.

NAPL in Water Experiments

After completing the soil testing program, 0.05 mL of kerosene, chlorobenzene, and tetrachloroethene were added individually to 40 mL of water in three 50-mL centrifuge tubes. A blank sample was prepared using 40 mL of water and no NAPL. The samples were visually examined after (a) the initial mixing, (b) centrifugation at 1250 rpm for one minute, (c) adding approximately 2 mg of Sudan IV dye, and (d) centrifugation of the dye-fluid mix at 1250 rpm for one minute. The two investigators evaluated the presence and relative density of NAPL in the samples.

Results

Soil Tests

Examination results for all soil samples and methods are provided in the Appendix, summarized in Table 2, and illustrated without distinguishing between different types of NAPL and soil in Figure 2. Organic vapor concentrations detected as a function of NAPL type and saturation are plotted in Figure 3. A measure of correlation between samples and ordinal ratings for

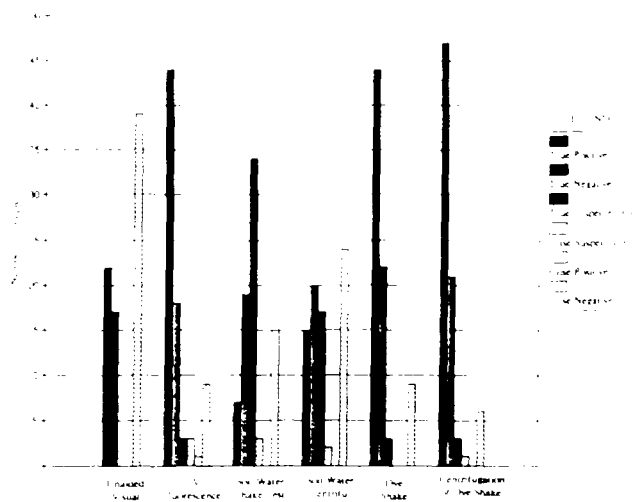


Figure 2. Determination outcomes by examination method.

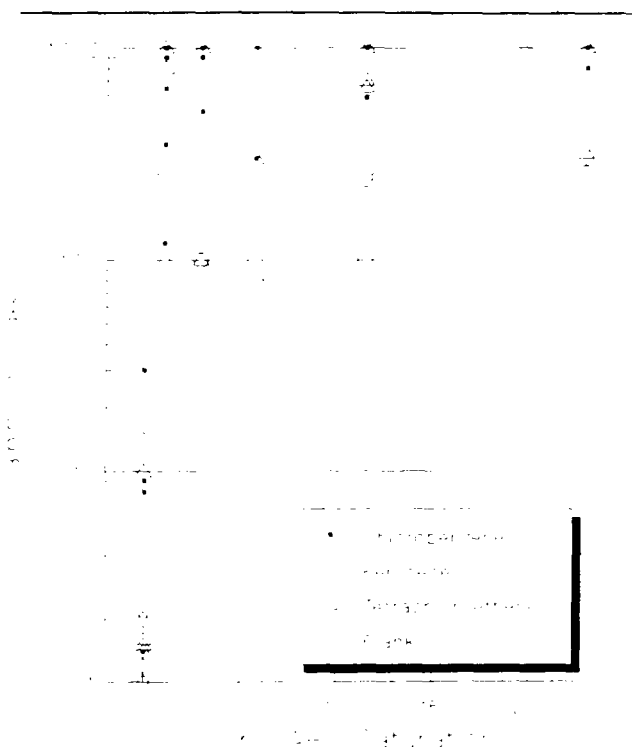


Figure 3. OVA concentrations plotted as a function of NAPL type and saturation. OVA measurements shown as 1000 ppm are actually >1000 ppm. Dissolved contaminant samples are treated as 0 percent NAPL saturation samples.

NAPL presence was developed to help assess the utility of the different examination methods. The correlation measure (CM) was calculated by (1) using the standard parametric correlation coefficient equation (Davis 1973); (2) setting the independent variable to 1 or 0 for samples with and without NAPL, respectively; and (3) setting the dependent variable to 1, 0.75, or 0 for A, B, and C NAPL presence ratings, respectively. Calculated measures of correlation between NAPL presence and examination method rating for all samples and for samples grouped by NAPL and soil type are given in Table 3. The correlation measure will equal 1.0 for a method with perfect determinative results (i.e., each sample with NAPL is given an A rating and each sample without NAPL is given a C rating). Conclusions regard-

TABLE 4
Examination Results for NAPL in Water Samples
(A = NAPL presence apparent based on visual examination; B = NAPL presence suspected based on visual examination; C = no evidence of NAPL presence; l = LNAPL; d = DNAPL.)

Sample	Visual Exam	Centrifugation Exam	Hydrophobic Dye Shake Test	Hydrophobic Dye Centrifugation Exam
0.05 mL of kerosene in 40 mL of water	B	C	A(l)	A(l)
0.05 mL of tetrachloroethene in 40 mL of water	B	C	A(d)	A(d)
40 mL of water	C	C	C	C
0.05 mL of chlorobenzene in 40 mL of water	B	C	A(d)	A(d)

dye shake test, was particularly effective with the medium sand samples (CM = 1.00). Overall, this combined procedure provided the most accurate results of the visual methods tested to determine NAPL presence in soil (CM = 0.81).

- The ease of determining NAPL presence in soil is directly related to the magnitude of visual contrast between NAPL, water, and soil. The visual contrast afforded by using hydrophobic dye to tint NAPL red is generally greater than that provided by UV fluorescence and much greater than that associated with the interfacial characteristics of colorless immiscible fluids. Of the methods tested, therefore, the hydrophobic dye techniques, followed by UV fluorescence, most facilitated the determination of NAPL presence in the soil samples.
- We recommend that dye shake tests be made in plastic containers (e.g., polypropylene tubes) because hydrophobic NAPLs generally wet plastic better than glass, thereby enhancing NAPL detection on the container wall.

Water Tests

Examination results for the four NAPLs in water samples are given in Table 4. During the unaided visual examination, the presence of NAPL was suspected in each of the three samples with NAPL, but not in the blank, due to the contrast of fluid characteristics at the fluid-air interface. Phase separation caused by centrifugation eliminated this contrast and the visual evidence of NAPL presence. Mixing hydrophobic dye with the samples instantaneously revealed the presence and density relative to water of the 0.05 mL of kerosene, chlorobenzene, and tetrachloroethene present in the three contaminated 40-mL samples (volumetric NAPL content = 0.125 percent). Subsequent centrifugation separated the dyed NAPL from the clear water, thereby facilitating determination of the volumetric NAPL to water ratio in a graduated centrifuge tube.

Conclusions

Of the methods investigated, the hydrophobic dye methods, followed by UV fluorescence (for fluorescent NAPLs), offer the most simple, practical, and effective means for direct visual identification of clear, colorless

NAPL in contaminated soil samples. These methods can be utilized in the field or in a lab with minimal time and material expense. Known background and NAPL-contaminated samples should be examined in addition to unknown samples, where possible, to check for interferences and site-specific NAPL responses. For volatile NAPLs, analysis of organic vapors in soil sample headspace can be used to screen samples for further examination and, possibly, to infer NAPL presence. The NAPL in water experiments demonstrates that the presence of very small quantities of clear, colorless NAPL in water can be quickly identified by mixing in a tiny amount of hydrophobic dye.

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Appendix. Formulation of Soil Samples and Examination Results. (Cont.)

Sample Number	Soil Type	NAPL Type	NAPL Volume Input (mL)	Estimated NAPL Saturation (%)	OVA Concentration (ppm)	Visual Exam	Fluorescence Exam	Shake Text Exam	Centrifugation Exam	Hydrophobic Dye Shake Test Exam	Hydrophobic Dye Centrifugation Exam
34	SAP	CB	dissolved	0.00	9	C	C	B	C	C	C
35	TS	CB	dissolved	0.00	8	C	C	C	C	C	C
36	MS	K	dissolved	0.00	6	C	B	C	C	C	C
16	SAP	K	dissolved	0.00	6	C	C	C	C	C	C
53	TS	K	dissolved	0.00	14	C	C	C	C	C	C
27	TS	K	dissolved	0.00	2.2	C	C	C	C	C	C
4	MS	PCE	dissolved	0.00	1.5	C	C	C	C	C	C
21	SAP	PCE	dissolved	0.00	10	C	C	C	C	C	C
70	TS	PCE	dissolved	0.00	1.6	C	C	C	C	C	C
20	MS	CB	0.35	1.00	120	C	C	C	C	A(d,m)	A(d,g)
19	MS	CB	0.35	1.00	350	C	C	C	C	A(d,m)	A(d,g)
35	SAP	CB	0.35	1.00	640	C	A	B	B	C	C
43	SAP	CB	0.35	1.00	>1000	C	A	B	C	B	A(d,g)
78	TS	CB	0.35	1.00	900	C	C	C	C	C	C
72	MS	K	0.35	1.00	150	C	A(z)	B	B	A(g)	A(l,g)
75	SAP	K	0.35	1.00	60	C	A	C	B	C	B(l,trace)
11	TS	K	0.35	1.00	300	C	C	B	B	C	C
69	MS	PCE	0.35	1.00	800	C	C(z)	C	C	A(d,g)	A(d,g)
3	SAP	PCE	0.35	1.00	>1000	C	C	C	C	B	C
51	TS	PCE	0.35	1.00	100	C	B	C	C	C	C
73	MS	CB	1	2.86	>1000	C	A	C	C	A(d,a)	A(d,m)
2	SAP	CB	1	2.86	500	C	A	A	B(L)	C	A(d)
57	SAP	CB	1	2.86	>1000	C	A	B	B	A(g)	A(d,g)
40	SAP	CB	1	2.86	900	C	A	C	C	A(g)	B(g)
66	TS	CB	1	2.86	>1000	C	A	C	C	A(m)	A(d,m)
68	MS	K	1	2.86	200	C	A(z)	B	A	A(g)	A(l,1 mL)
24	SAP	K	1	2.86	100	C	A	B	B	B	A(d,m)
22	TS	K	1	2.86	200	C	A	A	B	C	A(d,trace)
31	TS	K	1	2.86	50	B(s)	A	B	A	A(m)	A(l,m)
56	MS	PCE	1	2.86	80	C	C(z)	C	C	A(d,m)	A(d,m)
54	SAP	PCE	1	2.86	100	C	C	B	B	A(g)	B(g)
58	TS	PCE	1	2.86	>1000	C	B	B	C(x)	C	C
55	MS	CB	2	5.71	300	C	A	C	B	A(d,a)	A(d,a)
9	MS	CB	2	5.71	>1000	C	C	B	C	A(d,a)	A(l,a)
61	SAP	CB	2	5.71	>1000	C	A	B	B	A(g)	A(d,g)
25	TS	CB	2	5.71	>1000	B(s)	A	C	C	A(d,a)	A(d,m)
74	MS	K	2	5.71	80	C	A	B	A	A(l,m)	A(l,1/2mL)
1	SAP	K	2	5.71	100	B(s)	A	B	A(L)	C	A(l,g)
33	SAP	K	2	5.71	60	B(s)	A	B	A	A(m)	A(l,m)
76	TS	K	2	5.71	140	C	A	B	B	A(m)	A(l,g)
44	MS	PCE	2	5.71	300	C	B	B	C	A(d,a)	A(d,a)
23	SAP	PCE	2	5.71	200	C	A	B	A	A(d,m)	A
48	TS	PCE	2	5.71	300	C	A	B	C	A(d,m)	A(d,m)
62	MS	CB	4	11.43	580	C	A	B	C	A(m)	A(d,m)
59	SAP	CB	4	11.43	>1000	B(s)	A	B	B	A(m)	A(g)
45	TS	CB	4	11.43	>1000	C	A	B	C	A(d,a)	A(d,a)
67	MS	K	4	11.43	250	C	A	C	A	A(l,m)	A(1.2mL)
6	SAP	K	4	11.43	100	B(s)	A	B	A	A	A(1,m)
5	SAP	K	4	11.43	240	B(s)	A	B	A	A	A(l,g)
28	TS	K	4	11.43	200	B(s)	A	A	A	A(m)	A(1.1mL)
65	MS	PCE	4	11.43	650	C	A	B	C	A(d,a)	A(d,a)
8	SAP	PCE	4	11.43	>1000	B(s)	A	B	A	A(m)	A(d,m)